s12.m34.p9 **Dynamics of Entropy Production of Disordered Materials.** <u>Moyuru Ochiai</u>[1], Riko Ozao[1] and Giulio Casati[2], [1]*Department of Electronics and Informatics, North Shore College of SONY Institute, 428 Nurumizu Atsugi, 243-8501 Japan,* [2]*Centro di Cultura Scientifica "Alessandro Volta", Villa Olmo, 22100 Como Italy. E-mail: tomcat@shohoku.ac.jp*

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We describe a new application of the theory of stochastic processes to a glass state with the purpose of making a lot of conventional studies discussed by irreversible thermodynamics easier to understand.

Glasses are out of equilibrium. A glass state is thus a kind of a relaxation process, so called a irreversible one which varies very slowly because molecules of glass are apparently kept frozen under glass transition temperature T_g. Two main problems are in this field. In a glass state, a thermodynamic entropy derived from the theory of thermodynamics, becomes different from the measured entropies, is one problem. Another one is that glasses have residual entropy, that is non zero zero-temperature entropy. Nernst's theorem does not work in this case.

In experiments the entropies are measured by heat flow, and this leads that entropy determined by cooling and heating shows lower and upper bounds respectively on the entropy defined by thermodynamics.

Thermodynamics explains the result as follows . In order to define the temperature of the system in non-equilibrium, we consider an isolated system composed of a glass and a heat bath, of which total entropy increases with time. This model described by thermodynamics provides the relation;

$$S_c(T_a) \leq S_{stat}(T_a) \leq S_H(T_a) \quad , \qquad (1)$$

where $T_a < T_g$. S_c, S_H are entropies determined by cooling and heating at Ta respectively. Equality satisfies an equilibrium state.

This report presents a new application of stochastic methods to a glass state introducing a master equation

$$\frac{dP_m}{dt} = \sum_n \left[W(m \leftarrow n)P_n - W(n \leftarrow m)P_m \right] \quad , \qquad (2)$$

where $W(m \leftarrow n)$ stands for a transition rate from a state n to m. Introducing a functional form of detailed balance of a probability flow for a glass in contact with a heat bath, and the idea of the relationship between a generalized force and its conjugate flux, we obtain

$$\frac{dS}{dt} \geq \frac{1}{T}\dot{Q} \quad , \qquad (3)$$

which provides the relation(1).

s12.m34.p10 **Crystal Structure of Incommensurate and Commensurate Modulated Phases of Ferroelectric [4-NH$_2$C$_5$H$_4$NH][SbCl$_4$].** <u>A. Pietraszko</u>[a], R. Czopnik, R. Jakubas[b], [a]*Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-950 Wroclaw, Poland,* [b]*Faculty of Chemistry, University of Wroclaw, Joliot Curie 14, 50-383 Wroclaw, Poland. E-mail: adam@int.pan.wroc.pl*

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4-aminopyridinium tetrachloroantimonate (III), [4-NH$_2$C$_5$H$_4$NH][SbCl$_4$] (abbreviation 4-APCA), is a member of the compounds family of general formula $R_aM_bX_{3b+a}$ (where R = organic cations, M = Sb, Bi, and X=Cl, Br, I). 4-APCA was found to exhibit the complex sequence of phase transitions, [1,2]. The high temperature paraelectric phase (I) of C2/c symmetry is dynamically disordered with respect to the positions of 4-aminopyridinium (4-AP) cations. At 304 K the phase transition of order-disorder type takes place and the incommensurate modulated structure appears with modulation wavevector $\mathbf{q}=\beta\mathbf{b}^*$ with $\beta=0.60$. The symmetry of this phase (II) is described by C2/c(0β0)s0 superspace group. On cooling β changes from 0.60 to 0.66 and at 270.5 K the paraelectric - ferroelectric phase transition leads to the commensurate ferroelectric phase (III) with $\beta=2/3$ and Cc(0β0) symmetry. From 248 K down to 240 K the incommensurate modulated polar phase (IV) of Cc(0β0) symmetry is observed with ß varying from 0.66 to 0.70. Below 240 K the modulation of the structure disappears and the non-polar phase (V) of P2$_1$/n symmetry is observed. In our studies it was employed the superspace approach to the structure of commensurate modulated ferroelectric phase. In the models of the intermediate phases harmonic approximation of the modulation waves was assumed, since only first order satellite reflections were observed in diffraction patterns. On the basis of the detailed structure determination of incommensurate and commensurate modulated phases of 4-APCA using JANA2000 it was established that positional modulation is present for Sb and Cl atoms. It appears that SbCl$_4$ groups are not significantly distorted under the modulation and behave approximately as rigid units in all modulated phases. In case of the 4-AP cations both positional and occupational modulations are present. The latter was suggested by the dynamical disorder of the cations in the high temperature phase. The important result which was obtained is that in the ferroelectric phase amplitudes of displacement waves for cations are significantly larger than in modulated phases II and IV. It leads to the large displacement of 4-AP cations with respect to SbCl$_4$ groups which seems to be the primary reason for the appearance of spontaneous polarization in ferroelectric phase. This structural feature is crucial to the understanding of the mechanism of the para-ferroelectric phase transition in 4-APCA, since specific heat studies clearly indicates displacive character of this transition, [2]. On this basis it may be concluded that ordering of cations in ferroelectric phase is minor factor which influence the value of the spontaneous polarization, c.f. [1].

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